Sveriges lantbruksuniversitet
Swedish University of Agricultural Sciences

Department of Aquatic Sciences and Assessment

Predictive modelling of metals in Swedish reference lakes

Frida Eriksson Nordbäck

Department of Aquatic Sciences and Assessment
• •
• •

Predictive modelling of metals in Swedish reference lakes

Frida Eriksson Nordbäck

Supervisor: Brian Huser

Assistant Supervisor: Stephan Köhler

Examiner: Lars Lundin

Credits: 30 hec
Level: Master
Course title: Independent Project in Environmental Science
Course code: EX0431
Programme/education: Soil and Water Management

Place of publication: Uppsala
Year of publication: 2016
Cover picture: Jenny Kristoffersson, 2011
Title of series:
Number of part of series:
ISSN:
ISBN:
Online publication: http://stud.epsilon.slu.se

Keywords: heavy metals, predictive modelling, reference lakes , environmental monitoring

Sveriges lantbruksuniversitet
Swedish University of Agricultural Sciences

Faculty of Natural Resources and Agricultural Sciences
Department of Aquatic Sciences and Assessment

Abstract

Metals are a natural part in our environment. Due to increased use of metals in our society the biogeochemical cycles of metals are being altered on local, regional and global scales. Metals can be emitted through direct use of some elements (Fe, Zn and Cu) or indirectly as a result of processes (e.g., burning of fossil fuels resulting in emission of V and Hg). Both the chemical and physical properties of the element affect the amount of metals distributed in the environment, but the main factor is the usefulness of an element for humans. (Mason, 2013)

To be able to evaluate an anthropogenic impact on a lake of pollutants like metals, reference conditions are needed. Background concentration is one type of reference condition, which can be separated into regional and a natural background concentration. E.g. in Sweden, 1860 is used as a reference year for acidification because the effect of acid deposition should have been at a minimum during this time period (SEPA, 2010).

The aim of this study was to create a model that could predict the natural background concentration of a metal in lakes based on easily measured variables such as TOC and pH. This was possible for Pb, Zn and Ni (if including sedimentation rate).The predicted background concentration in this study were higher for all three metals than the one currently used in the Swedish Environmental Protection Agency's standards. However, beyond this it was also possible to model the current concentration of Al, Cu, Cr, Co, Fe, Mn and V in the studied lakes.

Due to the fact that all lakes are to some extent affect by humans (through atmospheric deposition), using modelling approach can provide a better way to estimate the background concentrations in lakes and through that also a better estimation of the human impact.

Sammanfattning

Metaller är en naturlig del i vår miljö. På grund av ökad användning av metaller i vårt samhälle har de biogeokemiska cyklerna rubbats på både lokal, regional samt global nivå. Utsläpp av metaller kan ske genom direkt användande av ämnet (Fe, Zn och Cu) eller indirekt som resultat av en process (förbränning av fossila bränslen resulterar i utsläpp av V och Hg exempelvis). En metalls kemiska och fysiska egenskaper avgör hur den sprids i miljön, men den största faktorn är hur användbar den är för oss människor. (Mason, 2013)

För att kunna utvärdera hur stor antropogen påverkan som skett på en sjö krävs ett referens tillstånd. Bakgrundskoncentration är en typ av referenstillstånd som sedan kan delas in i regional och naturlig bakgrundskoncentration. Inom försurning av sjöar används exempelvis år 1860 som referensår i Sverige (SEPA, 2010).

Syftet med denna studie var att skapa en modell som kan användas för att förutspå koncentrationen av en metall i en sjö baserat på parametrar som TOC och pH, vilka är enkla att mäta och ingår i det nationella miljö övervakningsprogrammet. Detta var möjligt för Pb, Zn och Ni (om sedimentationshastigheten inkluderades i modellen). Resultatet visar att den modellerade backgrundskoncentrationen i denna studie var högre för samtliga tre metaller än de som för närvarande används i Naturvårdsverkets jämförelsevärden. Förutom dessa tre modeller kunde även koncentrationen av följande metaller modelleras: Al, Cu, Cr, Co, Fe, Mn and V.

Med anledning av att alla sjöar är till viss mån påverkade av det mänskliga samhället (exempelvis genom atmosfäriskt nedfall) kan detta tillvägagångssätt, att modellera den historiska koncentrationen, erbjuda ett bättre sätt att uppskatta den historiska bakgrundkoncentrationen i sjö och genom det också en bättre uppskattning på den mänskliga påverkan.

Populär vetenskaplig sammanfattning

Metaller är en naturlig och livsviktig del av vår levnadsmiljö, dock kan vissa vara giftiga i för höga koncentrationer. Vi påverkar metallernas biogeokemiska cykler på både lokal, regional och global nivå genom vårt användande av metaller i vårt. Utsläppen kan ske genom olika processer, vissa metaller genom direkt användning av dem (järn, zink och koppar) och andra metaller genom förbränning av fossila bränslen (exempelvis vanadin och kvicksilver). Metallernas kemiska och fysiska egenskaper påverkar hur ämnet reagerar efter utsläppet och hur det sprids i naturen (Mason, 2013).

För att kunna utvärdera den mänskliga påverkan på en sjö måste det finnas ett tillstånd att jämföra med, till detta används ett referenstillstånd. Det finns flera typer av referenstillstånd för metaller, ett sådant är bakgrundskoncentration. Bakgrundskoncentrationer kan i sin tur delas in i regionala och naturliga. År 1860 används exempelvis som referensår för försurning av sjöar i Sverige eftersom påverkan av sur deposition inte hunnit ge så stor effektvid den tidpunkten (SEPA, 2010).

Syftet med denna studie var att modellera den naturliga bakgrundskoncentrationen av metaller i svenska sjöar baserat på parametrar som ingår i det nationella övervakningsprogrammet (ex. pH och TOC). Detta var möjligt för bly, zink och nickel. För nickel krävdes det även att sedimentationshastigheten ingick i modellen. Resultatet från modellerna visade på högre bakgrundshalt för samtliga tre metaller jämfört med Naturvårdsverkets jämförelsevärden. Utöver dessa metaller var det också möjligt att skapa modeller som beskrev aluminium, koppar, krom, kobolt, järn, mangan samt vanadin. Dessa kunde tyvärr inte testas, inom ramen för denna studie, mot uppmätta halter från de studerade sjöarna.

Då alla sjöar är påverkade av oss människor genom atmosfäriskt nedfall kan detta arbetssätt, att skapa modeller för bakgrundskoncentrationer av metaller i sjöar, vara ett bättre arbetssätt för att utvärdera hur stor den mänskliga påverkan är istället för som i dagsläget; använda koncentrationer från sjöar som bedöms vara mindre påverkade.

Contents

1 Introduction

Metals are found in all lakes, having both natural and anthropogenic origins. To be able to estimate the anthropogenic influence on a lake, a reference condition is needed to compare with. A reference condition is an estimation of what the concentration would be with no human impact (background concentration). In today's monitoring the background concentration used for environmental assessment of lakes in Sweden is based on the 50-percentil value for lakes found in a specific region (ecoregion) (Johansson et al., 2009).

Modelling has been used in environmental science for long time, especially when working with eutrophication or acidification of surface waters (Lindström, 2000). Through mathematic formula, it is possible for a researcher to describe relationships in nature. Predictive modelling can forecast scenarios both in future and historical time periods through applying formulas based on current and/or historical data to new scenarios. Predictive modelling of metals has been used in earlier research to estimate the load of metals reaching a lake, concentration in sediment and the distribution of metals between particulate associated and dissolved fractions (Lindström, 2000). However, it has not been used to predict the concentration of a certain metal in lake water.

Total organic carbon (TOC) is one of the factors affecting metal concentration in a lake both directly and indirectly. Observations in recent years, together with modelling, have shown an increase of TOC in both rivers and lakes (Cunningham et al, 2008, Rosén, 2005). Increasing TOC in lakes could potentially increase the metal concentration in the water. This together with the fact that the reference condition used today is based on measurements made in the last 30-years, urge for the need of a new method to estimate background concentration.

1.1 Aim

The aim of this study was to construct a model able to predict background concentrations of metals in Swedish lakes. This was done through an empirical model based on sediment and water chemical data. The hypothesis to be answered is if it is possible to predict background metal concentrations based on readily available historical data such as TOC, pH and sediment metal content.

1.2 Limitations

The metals studied are those included in the Swedish Freshwater monitoring program except for Mercury (Hg), Cadmium (Cd) and Arsenic (As). These three are excluded from this study due to limitations in analysing methods (ICP-AES and ICP-MS). Remaining metals that are used in this study are Aluminium (Al), Copper (Cu), Chromium (Cr), Cobalt (Co), Iron (Fe), Manganese (Mn), Lead (Pb), Nickel (Ni), Zinc (Zn) and Vanadium (V). The factors used in the modelling were pH, TOC, sedimentation rate and concentration of metals in sediment.

2 Theoretical framework

Metals are natural parts of aquatic ecosystems. Some are essential to living organism, but can still be toxic at high concentrations. Due to increased use of metals in daily life, biogeochemical cycles are being altered on both local, regional and global scales (Nriagu and Pacyna, 1988). Metals can be emitted through direct use of some elements (Fe, Zn and Cu) or indirectly as a result of processes (e.g., burning of fossil fuels resulting in emission of V and Hg). Both the chemical and physical properties of the element affects the amount of metals distributed in the environment, but the major factor are the usefulness of an element for us human being (Mason, 2013).

2.1 Reference conditions

To be able to evaluate an anthropogenic impact on a lake, reference conditions are needed. Background concentration is one type of reference condition, which can be separated into regional and a natural background concentration. E.g. in Sweden, 1860 is used as a reference year for acidification (SEPA, 2010).

The natural background concentration of a certain metal is the concentration that is assumed to be present in a lake without any human impact, while the regional background concentration takes diffuse inputs into account (e.g. nitrogen- and sulphur oxides from burning of fossil fuels) (Stoddard et al., 2006). The regional background concentrations in Swedish lakes are calculated as the median concentration of all measured values in the same limnological ecoregion with the same hydromorphological properties (Johansson et al., 2009).

In July 2000 the water framework directive was established, forcing the member countries to monitor surface water bodies. The aim with the objective is to work for a sustainable use of water in our society. Metals concentrations in lake ecosystems are parts of this work through the evaluation and monitoring of chemical status of surface waters (“2000/60/EG,” 2000; “Övervakning enl. vattendirektivet,” n.d.).

2.2 Metals in the environment - sources and impact from pollution

Emission of metals to the environment takes place from all types of combustion processes, transport, mining, agriculture, waste treatment, cement production, and metallurgic industries. The form of emission (gas, particulate e.g.) specifies the impact. Point source output from an industry close to a water body impacts the local

area, whereas air emission are diffuse and can spread longer distances. A majority of metals are emitted and transported as particles in the atmosphere. Hg is an example of a metal where transport can take place in gaseous form (Mason, 2013). Depending on the chemical and physical properties, together with characteristics of the source (height over ground, local environment such as wind and topography), distribution patterns differs between metals

Metals are transported according to weather patterns and deposited in wet and/or dry deposition. In Sweden, a major part of the atmospheric deposition of heavy metals originates from outside the country. Studies of mosses have shown that the atmospheric deposition of heavy metals is distributed in a geographically (spatially) decreasing gradient from south to north in some part of the Sweden (Rühling and Tyler, 2001, 1971). These studies also show that the deposition of metals has decreased since approximately 1968/70. Especially for Fe and Pb, which in 1995 were 20% and 11% of the values measured in 1968, respectively. The decreases may be explained by actions taken to reduce long-range transport of particles.

2.3 Availability and transport of metals to lakes

The hydrogeochemical cycles of metals are the connecting pathways between water, land and atmosphere. Metals can enter the hydrological cycle through natural processes, such as weathering and erosion, or by emission with anthropogenic origin (Håkanson, 1983; Mason, 2013). The amount of metals reaching a lake is influenced by factors such as size of the lake, the catchment size and land use.

2.3.1 Classification of metals

Different classification concepts can be used to better predict how metals will behave in the environment. One common way to classify metals is to categorize them based on the number of electrons in the outer orbital shell with the classes A-, B- or C-type. The A-type metals have an electron configuration causing low polarizability, whereas B-type metals have a high polarizability. C-type metals have partially filled outer orbitals (Mason, 2013). Another method used is to differentiate them into hard and soft metals, similar to hard and soft acids and bases. The term hard and soft originates from how easily the electron shell is deformed by influence of other ions (Mason, 2013; Stumm, 1996).

Based on these two concepts, it is possible to make simple predictions of how stabile different complex formations are. Soft metals typically form complexes through covalent bonding with soft ligands while hard metals forms ionic bonds with hard ligands (Mason, 2013). Complexes consisting of both hard and soft metal –ligands can also be formed but will not be as strong as hard-hard or soft-soft complexes. Complexation is described further in section 2.4.1 *Complexation*.

Table 1. *Based on Stumm (1996) showing the allocation between A-type, B-type and transition metal cations (Stumm, 1996). The metals studied are marked with bold font*

Hard/A-type metal cations	Transition metal cations	Soft/B-type metal cations
Li^{+}, Na^{+} , K^{+}, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Al^{3+}, Sc^{3+}, $La^{3+,}$ Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}	**V^{2+}**, **Cr^{2+}**, **Mn^{2+}, Fe^{2+}, Co^{2+}**, **Ni^{2+}**, **Cu^{2+}**, Ti^{2+}, **V^{3+}**, **Cr^{3+}**, **Mn^{3+}**, **Fe^{3+}**, **Co^{3+}**	**Cu^{+}**, Ag^{+}, Au^{+}, Tl^{+}. Ga^{+}, **Zn^{2+}**, Cd^{2+}, Hg^{2+}, **Pb^{2+}**, Sn^{2+}, Tl^{3+}, Au^{3+}, In^{3+}, Bi^{3+}

2.4 In-lake metal cycling process and availability

The effects of metals on a lake ecosystem are determined by the speciation of the metals. Speciation is the distribution of a metal between different forms, for example free ion (Fe), Fe-colloids and Fe complexes in solution. To separate soluble from particulate forms, a membrane filter with a size of 0.45µm is generally used (Berggren Kleja et al., 2006). Through this filtration the metals in the lake can be divided into adsorbed, colloidal and dissolved metals. Processes that control the speciation are interactions with particles (sorption), complex formation and biological uptake. Environmental parameters that affect these processes in lakes are pH, redox potential, temperature, residence time, alkalinity and dissolved oxygen among others (Håkanson, 1983; Stumm, 1996). This section will go through some of the processes affecting the metal concentration and distribution in both the water column and the sediment in the lake.

2.4.1 Complexation

Complexation is an important process when studying trace metals in aquatic systems. A complex consists of a combination of separate atoms/ions; a metal ion called the central ion that binds to another atom called ligand. Ligands can be single ions and molecules, such as EDTA, or organic molecules. The formation of a complex can take place both between soluble free ions and between a free ion and a surface area forming a surface complex (Berggren Kleja et al., 2006). Depending on

which type of metal and ligand is present, stability of the complex may differ. Hard metals prefer ligands with oxygen as an electron donor while soft metals prefer ligands with N or S as a donor atom (Stumm, 1996).

2.4.2 Adsorption- desorption

Lake sediment is generally a sink for metals in the environment due to physical and chemical adsorption. Metal ions are bound to particles that settle and accumulate at the bottom of the lake. Clay minerals, oxides, and solid organics are the most important adsorbents or sorbents, but colloids are also important (Kretzschmar and Schafer, 2005; Sparks, 2005). Both complexation and adsorption processes are dependent on pH and surface charge of the particle.

2.4.3 Interactions with organic matter

Organic matter in a lake can be produced within the lake (autochthonous) or transported to the lake from the surrounding landscape (allochthonous) (Håkanson, 1983). Organic matters influence metal concentration both in the dissolved and solid forms. Uptake of metals, through physical or chemical adsorption by solid organic matter, influences the distribution and the amount of metals retained in the sediment (Hart, 1982). Changes in dissolved organic carbon (DOC) also have an effect on the physical, chemical and biological parameter in the lake. An increase in DOC can create a shift in the distribution of thermocline layers in a stratified lake (due to decreased amount of light) (Pérez-Fuentetaja et al., 1999). Oni et al (2013) refer to a variety of research showing that DOC impacts the toxicity, speciation and mobility of metals such as lead (Pb), copper (Cu) and cesium (Cs). Through its capacity to bind protons, DOC also affects the pH, which can cause a shift in the redox properties of different ligands in the lake.

2.4.4 Internal load/Redox transformation

Metals in the sediment can re-enter the water column through re-suspension or release at the sediment-water interface. Fe and Mn are two metals that participate in redox processes in aquatic systems (Stumm, 1996). The availability of oxygen generally controls this type of chemical reaction. If the water above the sediment has low oxygen concentration, and no other alternate electron acceptors are available (e.g. NO_3^- or SO_4^{2-}), the reduction of Mn and Fe will take place at the surface of the sediment. When $Fe(OH)_3$ (s) are reduced at the sediment surface to Fe^{2+}, it becomes re-dissolved and enter the water column again (McBride, 1994).

The sensitivity to changes in redox condition varies between metals. Fe and Mn are two elements that are more sensitive than others, causing the capacity to migrate within the sediment (pore-water). This can results in a layer with higher concentration of the two oxides at the sediment surface. Example of metals that are not redox sensitive are Al and Pb (Boyle, 2001). However, these processes are influenced of if the lake is stratified or not. In a stratified lake there will be oxygen depletion in the hypolimnion during summer/winter which can cause reduction of Mn and Fe and release from the sediment (Mason, 2013).

2.4.5 Impact of biological activity

Different forms of a specific metal in lake water (or aquatic systems) include dissolved and particulate/colloidal metals in the water column and the sediment. Connecting these pools are the uptake by phytoplankton (as the first step in the food chain) and decomposition of detritus (Hart, 1982). Uptake can be divided into two types. The first results in retention or incorporation of metals into particulate matter, and when the plankton die, the metal will be released after the organic matter is mineralized by bacteria. The second type of uptake transforms the metal into different species. Methylation is one of the latter forms, where an atom is replaced with a methyl group. B-type metals (e.g. Pb, Hg and As) are generally those that can be methylated. This type of transformation increases the toxicity and biomagnification of e.g. mercury (as methylmercury). (Mason, 2013)

2.5 Modelling of metals in lakes

Lindström (2000) describe the criteria for a good predictive model of heavy metals in a lake. A model should be general, in that it is possible to apply it to all types of lakes. It should also be constructed with easily measured driving variables and be possible to be empirical tested. The size of the model, in terms of number independent variables, is important when building a model. Every independent variable added brings a certain uncertainty to the model, at the same time as the coefficient of determination increases (r^2-value). Håkansons advice, when building predictive dynamic or statistical regression models, is to use between two to six variables describing the dependent variable (Håkanson, 1995).

2.6 SEPA's water quality standards

Swedish Environmental Protection Agency has developed guidelines for concentration of metals in water and sediment on both national and regional scales to be used as a reference value for how affected a lake is by anthropogenic disturbance. Both a natural concentration and a regional background concentration are used to evaluate lakes. For water concentration, the estimated natural concentration is based on lakes in the northern parts of Sweden with low impact from atmospheric deposition. The regional background concentrations are based on groups of lakes classified from geographical location (limnological ecoregion) and surrounding conditions. (Johansson et al., 2009; Wiederholm, 2000)

Table 2. *Table based on the comparison value set by SEPA for non-acid lakes (pH>6) (Wiederholm, 2000). Sediment concentrations are given as dry weight. Natural concentration are based on lakes with low anthropogenic impact in the north of Sweden, while background concentration are based on lakes divided into groups regarding geographical location (limnological region), hydromorphological characteristics and watershed conditions (Johansson et al., 2009)*

	Cu	Zn	Cd	Pb	Cr	Ni	Co	V
Lakes (µg/l)								
Natural	0.3	1	0.005	0.05	0.05	0.2	0.03	0.1
Background North Sweden	0.3	0.9	0.009	0.11	0.05	0.2	0.02	0.1
Background South Sweden	0.5	2.0	0.016	0.24	0.2	0.4	0.06	0.2
Sediment (mg/kg)								
Natural	15	100	0.3	5	15	10	15	20
Background North Sweden	15	150	0.8	50	15	10		20
Background South Sweden	20	240	1.4	80	15	10		20

3 Materials and Methods

To better describe the modelling process used in this study, a process tree describing each step in constructing the models is presented below (Figure 1).

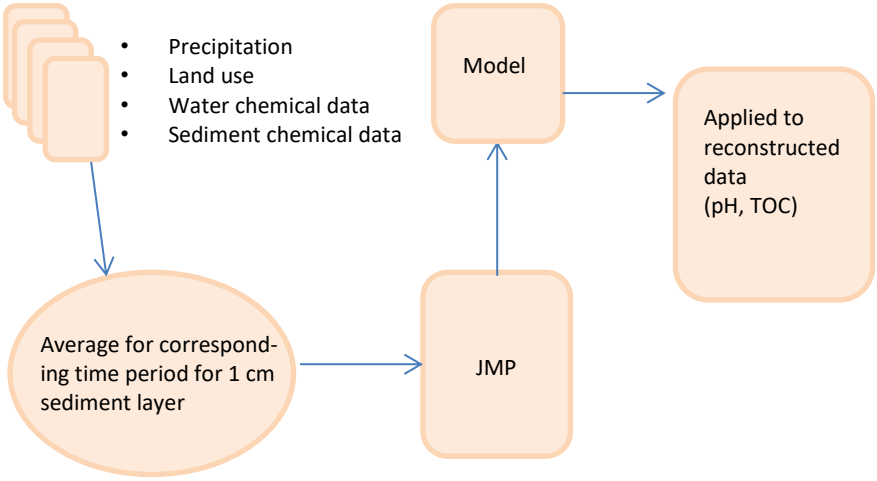


Figure 1. Process tree describing the work in this study. Averages for time periods corresponding to 1 cm of sediment layer were calculated from the collected data. These averages were used in the modelling software JMP to create models describing metal con-centration in the lake water. The models were then applied to reconstructed data such as pH and TOC to predict historical concentrations

3.1 Study sites

The study contains 17 lakes which all are part of the long-term national monitoring program in Sweden (Fölster et al., 2014). The lakes are used as reference lakes meaning that they have not been limed, are not affected by point source pollution, and minimal changes to land use have occurred (Swedish Environmental Protection Agency, n.d.). The lakes are distributed over most part of Sweden except the county of Norrbotten (*Figure* 2).

Figure 2. Situation map over the lakes used in this studied

3.2 Data collection

Climatic data (i.e., precipitation and temperature) were collected from the Centre of Environmental Data Archival (Climatic Research Unit (CRU) time-series datasets for variations in climate with variations in other phenomenon, and cover the time span 1901-2013 (CRU, 2008).

Water chemical data were downloaded from the Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Sciences and is a part of the national freshwater monitoring program. Surface samples varied from a depth between 0.5-2 m. The number of samples per year increased when the program was expanded. The oldest data consists of between one to three samples per year (1983), whereas later the sampling interval increased to up to six to eight times per year (metals were not measured each sampling event).

Sediment cores were collected in 1998,1999, 2006 and 2014 (Table *3*) as a part of the national environmental monitoring program and a recent Formas project (LIMT, Huser, 2012). Six cores, three old (1999) and three new (2014) were analysed for metals to increase the time period with overlapping data points.

The age of the sediment was determined, as part of earlier projects, at Umeå University at the Department of Ecology and Environmental Science through using ^{210}Pb method (Appleby and Oldfield, 1978; Olid et al., 2014).

Table 3. *Geographical and morphological data for the studied lakes. X means data were not available*

Lake	N	E	Catchment area (km^2)	Lake area (km^2)	Water residence time (y)	Lake volume (km^3)	Mean depth (m)	Max depth (m)	Sediment sampled
Allgjuttern	6423441	564895	1.1	0.16	3.46	0.70	5.13	13.72	1999
Djupa Holmsjön	6561755	615611	1.6	0.14	1.33	0.38	3.17	8.20	1998
Grissjön	6513623	508222	1.6	024	1.88	0.84	4.25	11.60	1999, 2014
Harasjön	6319105	413711	5.6	0.57	0.81	1.63	3.45	10.09	1999, 2014
Hällsjön	6319105	413711	1.5	0.21	1.47	0.65	3.73	10.08	1998, 2006
Remmarsjön	7085766	660807	125.7	1.35	X	X	5	14	1999
Rotehogstjärnen	6524402	304387	3.6	0.17	0.16	0.46	3.71	8.62	1999, 2014
Siggeforasjön	6650914	620487	21.5	0.7	0.44	2.13	3.17	10.97	1998, 2006
Stora Envättern	6555228	634745	1.4	0.38	4.02	1.03	3.25	9.02	1998
Stora Gryten	6526890	562305	19.1	1.06	0.63	2.86	1.60	10.03	1999, 2006
Svartesjön	6302133	392431	0.4	0.03	0.26	0.05	2.88	2.62	1999
Svinarydsjön	6225833	496102	1.8	0.18	1.44	0.47	4.13	7.64	1999
Tväringen	6901492	534982	36.2	1.61	0.45	5.32	5.48	12.77	1998
Tärnan	6606900	690200	13.5	1.06	1.92	4.82	4.26	16.16	1998
Älgsjön	6551428	578455	5.0	0.35	1.12	1.25	4.04	11.96	1998
Örsjön	6237996	480506	0.9	0.19	4.12	0.64	3.71	10.85	1999
Övre Skärsjön	6633397	530845	8.8	1.7	1.63	5.07	3.71	11.66	1999

The pH data used are yearly mean values from measured samples during the period 1983-2013. When no water chemical data were available, modelled values between 1860-2100 were used (generally only needed before 1980). The modelled pH was estimated with the MAGIC model (Model of Acidification of Groundwater In Catchments). MAGIC is a parameter model developed to estimate soil and water acidification (Cosby et al., 1985a, 1985b, 1985c). Based on Futter et al. (2014) the values 3.8, 4.7 and 5.5 was used for pKa_1, pKa_2 and pKa_3 respectively.

3.3 Chemical analysis and calculations

Sediment samples were freeze-dried after freezing at -20 C for 24 hours to calculate the water content. To extract metals, sediment was exposed to distilled HNO_3 (7M) and autoclaved at 121°C for 30 min. The samples where then centrifuged and two dilutions were made (depending on the metal) with a factor of 10 (Fe, Al) and 100 (all other metals). ICP-AES was used to analyse the extractions. Calibration of the machine was performed by the staff at the Chemistry Department at Uppsala University using a standard from Spectra Scan. Blanks were treated and analysed identically to the samples.

The method used in the monitoring program to determine metal concentrations was ICP-MS. To be able to increase the amount of data with low economical cost, ICP-AES was chosen as analysing method in this study. To ensure that it would be possible to compare result from ICP-AES with ICP-MS, replicates were made from old samples (from earlier research project using ICP-MS) to see if the result differed (Table 4). The difference between ICP-AES and MS was highest for Cd and As (Table *4*). Zn also showed substantial difference for samples from core Brunnsjön-2, where the result from ICP-AES was 51% higher than with ICP-MS. The sediment from Pahajärvi showed high difference for all metals measured. Based on the above results, however, Cd and As were excluded from the analysis.

Table 4 .*The table shows the percentage of difference between analyses made with ICP-AES and ICP-MS. Original data is found in Appendix 1* - Table 14

Lake	Al	Fe	Mn	Cu	Zn	Pb	Cd	Cr	Ni	Co	As	V
Brunnsjön-1	8	11	18	1	20	1	68	8	10	2	75	6
Brunnsjön-2	3	3	1	5	51	1	92	8	14	13	95	16
Bysjön	13	5	6	13	5	5	61	19	22	5	27	23
Pahajärvi	19	17	19	22	3	19	370	28	30	25	6	32

3.4 Data analysis

Water chemical and sediment data were $\log_{10}$ transformed to normalize distributions. Averages of the water chemical data, during corresponding time periods for each sediment layer, were calculated along with precipitation. For example, if the

sediment sample from 0 to 1 cm sediment depth contained 10 years of deposited sediment, water and climatic data were averaged over this same 10-year period.

The data were analysed through stepwise multiple regression, to see which of the variables influenced the metal concentration the most. As a second step, the data was divided into groups based on ratio between watershed area and lake area, pH, and by the morphometric index created by Osgood. The Osgood Index uses the ratio between the mean water column depth and the square root of the lake area to predict if water column mixing occurs in the lake during summer. A value less than 6 classifies the lake as shallow (indicating that it may be polymictic) and higher than 8 as less prone to mixing, or stratified. (Cooke et al., 1993)

The ratio between watershed and lake area (WS: LA) was used as an indicator for amount of surface runoff reaching the lake relative to lake size. A high ratio (small lake area and large watershed) can result in greater amount of watershed derived metals reaching the lake through surface flow whereas direct deposition of metals may be more important for lakes with small watershed. Three divisions were created to separate lakes with different WS:LA ratios: ratios either less 12.5, between 12.5 and 25, or greater than 25 were used as separation criteria.

Categories were also developed for the lakes based on pH, either acidic (<6) or non-acidic (>6) lakes based on. Some lakes have been classified as slightly acidic (pH between 5.5 and 6), but are counted as acid in the modelling part (Wiederholm, 2000).

3.5 Modelling

Multiple linear regression analysis was used to determine variables that had a strong influence on metal concentration in the lake water. This method assumes that the data satisfy a linear relationship, as example:

$$y = a + b_1 \, x \, X_1 + b_2 \, x \, X_2 + \cdots + b_n \, x \, X_n.$$

The X in the formula represent the independent variables and the *a* and *b* are regression coefficients (Grandin, 2013). The analyses were done with JMP statistical software (SAS Institute Inc., version 11). Forward stepwise regression was chosen as

modelling type, meaning that the analysis starts with no variables and then variables are added until the stopping criteria is fulfilled. As stopping criteria a BIC (Bayesian Information Criterion) value as low as possible together with a $p \leq 0.05$ was used. The aim with BIC value is to reduce the risk for over fitting the model by rectifying for each adding parameter.

The software (JMP) produces an equation with the most significant variables included (X_n). By using more than one independent variable in the model there is a risk for multicollinearity between the variables. A correlation analysis was made between variables used to minimize this risk. (Grandin, 2013)

As a first step the MLR analysis was made with all parameters to create more general models, as a second step the predictive models where developed based only on parameters that were possible to reconstruct historically. A residual analysis was made for Pb, Zn and Ni, to detect potential bias. In the results section adjusted r^2 values are presented. The adjusted r^2 value takes the amount of variables in the prediction formula into account (Grandin, 2013).

4 Results

The results are divided into two parts. The first part consists of models built with all available parameters (general models) and the second part contains models built with parameters with an historical record (either measured or predicted) such as pH, TOC, precipitation, sedimentation rate (predictive models). An R^2 value of 0.7 was chosen as a limit for presented results.

4.1 Variability of metals in water

The metal concentrations in surface water samples varied substantially between the lakes (Table 5). The concentration of Fe in Lake Harasjön was 2381 µg/l compared to Lake Allgjuttern 39 µg/l. In addition, Lake Harasjön was also higher regarding concentrations of Mn where it had the highest value of all lakes (233 µg/l). By looking at controlling variables such as pH and TOC, it possible to see that Lake Harasjön is acidic and TOC increased during the time period with available data (1994-2011).

Table 5. *Lake specific average of chemical data for studied lakes. TOC are given in mg/l while the metals are shown in µg/l. Overlapping time series of measured metals were not available for all lakes which is represented by empty cells*

	TOC	Al	Fe	Mn	Cu	Zn	Pb	Cr	Ni	Co	V
Allgjuttern	7.0	56	39	15	0.5	6.9					
Djupa Holmsjön	11.9	182	299	54	0.8	10					
Grissjön	11.7	252	326	26	0.4	5.5	0.7	0.3	0.5	0.2	0.4
Harasjön	16.8	255	2381	233	0.7	7.2	2.6	0.4	0.4	0.3	1.0
Hällsjön	8.6	102	232	45	1.3	4.6	0.2	0.2	0.3	0.1	0.2
Remmarsjön	9.3	166	627	35							
Rotehogstjärnen	12.6	292	542	50	0.6	7.2	0.7	0.4	0.9	0.7	0.6
Siggeforasjön	15.8	209	483	91	0.9	5.0	0.3	0.4	0.4	0.1	0.6
Stora Envättern	8.6	51	45	11							
Stora Gryten	17.2	142	357	99	1.0	2.6	0.5	0.4	0.9	0.2	0.5
Svartesjön	15.3	155	1750	39							
Svinarydsjön	9.2	221	319	99							
Tväringen	8.0	69	215	29	3.1	5.8					
Tärnan	9.1	54	90	21							
Älgsjön	18.4	148	595	93							
Örsjön	7.3	119	352	144							
Övre Skärsjön	7.2	172	338	39	8.9	10					
Average	11	155	529	61	1.80	6.49	0.84	0.36	0.55	0.29	0.55
Max	18.4	292	2381	233	8.9	10	2.6	0.4	0.8	0.7	1.0
Min	7.0	51	39	11	0.4	2.6	0.2	0.2	0.2	0.1	0.2

The concentration of metals in a lake is affected by the surrounding land use of the catchment. Most of the lakes have forest dominated catchments (*Figure 3*). In contrast are Lake Örvattnet and Lake Stora Envättern, which have large parts of the catchment covered by open surface water. An exception is Lake Svartesjön, which has the highest percentage of wetland area together with the lowest area of forest cover.

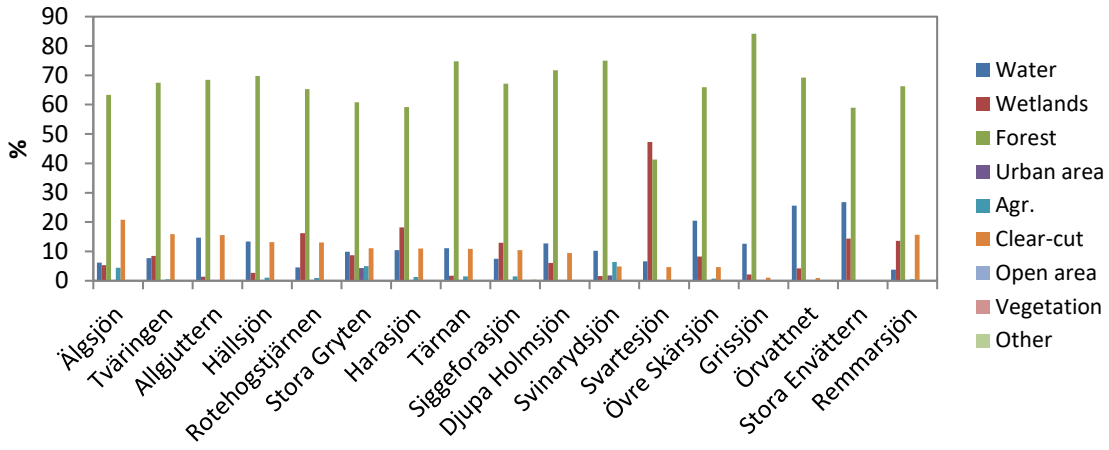


Figure 3. Percentage of land use for each catchment. Svartesjön stands out with more than half of the catchment area covered with wetlands. Lake Älgsjön has the highest percent of clear-cut area while Lake Svartesjön catchment has the highest cover of wetland.

4.2 General models

Multiple stepwise regression analysis resulted in nine models describing seven of the studied metals (Table 6). The p-value was less than 0.0001 for all models except for Ni ($p < 0.001$). The highest r^2 value achieved was for the model for Ni based on TOC, sedimentation rate, precipitation and iron concentration in the water column. TOC had the highest predictive effect on Fe, with an increase of 1.77 for each increase of one of $\log_{10}$ TOC (mg/l), and the lowest impact on the Vanadium model. Sedimentation rate had both positive (Fe and Zn) and negative (Ni) effects on some of the metals.

Table 6. *Result from the stepwise MLR analysis, showing independent variables used to describe different metal concentration the lakes (µg/l). The numbers in the columns are the coefficients for each specific variable (pH, TOC, sedimentation rate etc.). TOC data were log_{10} transformed before constructing the models. Sediment concentrations (mg/kg) are given as dry weight. N represents number of data points used in the model*

Metal	r^2	P	N	Inter-cept	pH	TOC (mg/l)	Sed rate (cm/y)	Preci-pitation	Fe (sed.)	Cr (sed.)	Al (sed.)	Fe (wat.)	Al (wat.)
Al	0.63	<0.0001	50	-0.39	-0.24						0.767	0.298	
Fe	0.78	<0.0001	44	-1.00	-0.35	1.77	0.38	0.00105	0.64				
Zn	0.47	<0.0001	27	3,03	-0,4								
Zn	0.79	<0.0001	20	8.83	-1.03	1.53	0.86			1.53			-1.95
Pb	0.79	<0.0001	21	0.39	-0.41	1.57							
Ni	0.73	<0.001	15	-1.64		1.40	-0.75						
Ni	0.94	<0.0001	15	-5.88		1.36	-0.66	0.00082			1.36		
Co	0.71	<0.0001	21	3.31	-0.61	1.17						-0.59	
V	0.87	<0.0001	15	2.76		0.97	0.54		-0.94				

A multivariate analysis was made to see if there were any correlation between the independent variables in the data (Appendices -Table 16). The analyse showed that V, Pb and Al are strongly correlated to Fe concentration in water, with *r* values of 0.79 for V and Pb and 0.69 for Al.

The next step was to analyse the data based on groups sorted by morphometric properties (represented by Osgood Index), acidity and WS:LA. The lakes contributes with between one data points up to 11 at most (specification in Appendices -Table *16*). The distribution was even between most of the categories except WS:LA which have less numbers lakes when the ratio increases (*Table 7*).

Table 7. *Summary of the distribution of lakes between groups. The distribution is even between the categories except for lakes with higher WS:LA than 12.5. These two groups consist of only 5 lakes each*

	Osgood Index		Acidity		WS:LA		
	Deep	Shallow	Acid	Neutral	<12.5	12.5–25	>25
Number of lakes	9	8	8	9	8	5	5

When analysing the lakes divided based on pH, the result consists of two models describing Al in acidic lakes and six models describing Fe, Mn, Ni, V, Cr and Pb in neutral lakes. All models have positive regression coefficients for TOC and only two models have pH as a driving variable (Table *8*). The number of data points used in Fe-model was highest with 30 data points, while the rest of the models were based on 13-14 data points.

Table 8. *The result of stepwise MLR made on acid and neutral lakes. The numbers are the coefficients used in the expression describing the concentration of a certain metal, resulting in one row builds one expression.* ***Sed*** *stands for sediment concentrations, class* ***NE*** *stands for neutral and class* ***A*** *for acid lake (pH<6).* ***N*** *represents number of data points used in the model*

Metal	Class	r^2	p	N	Intercept	pH	TOC	Sed rate	Precipitation	Fe (sed.)	Al (sed.)	Pb (sed.)
Fe	NE	0.85	<0.0001	30	-5.25		1.55			1.26		
Mn	NE	0.78	<0.0001	30	2.55	-0.50	2.24					
Ni	NE	0.97	<0.0001	13	-2.55		1.60	-0.50	0.000963			
V	NE	0.94	<0.0001	13	-2.24		1.49	0.34			0.22	
Cr	NE	0.82	<0.0001	13	-1.6		1.00					
Pb	NE	0.88	<0.001	13	-15.48	0.85	3.23	0.26				2.81
Al	A	0.79	<0.001	14	1.19			-0.53	0.000424		-0.94	
Al	A	0.69	<0.0001	14	2.10			-0.5	0.000435			

When using Osgood index to analyse the lakes, the number of data points included in the models decreased compared to earlier models, which may cause higher uncertainty in the results (*Table 9*). Eight models were constructed, describing seven metals in lakes with an Osgood Index of deep.

Table 9. *The result from multiple stepwise regression analysis made on the lake with Osgood index deep. Sediment values (mg/kg) are given as dry weight, TOC in mg/l and sedimentation rate in cm/y*

Metal	r^2	p	N	Inter-cept	pH	TOC	Sed rate	Precipita-tion	Fe (sed.)	Al (sed.)
Al	0.70	<0.0001	23	0.82	-0.33	0.60				0.64
Cu	0.95	<0.01	7	6.28		-4.85	-6.50			
Fe	0.9	<0.0001	19	-1.33	-0.55	1.67	0.95	0.0009209	0.97	
Mn	0.73	<0.0001	19	-1.69	0.79		-0.96			
Ni	0.90	<0.001	8	3.36	-0.63					
Pb	0.82	<0.01	8	3.33	-0.64					
V	0.84	<0.001	8	-1.58				0.001427		
V	0.96	<0.0001	8	4.34				0.0015081		-1.38

When analysing the lakes with an Osgood Index <6 (shallow lakes) eight models were possible to construct (*Table 10*). The metals described were the same as for deep Osgood Index except for Co instead of Cu. Common for these models are that none of them have precipitation as a predictive variable in contrast to the other groups. All models except three have a p-value <0.0001 and the model predicting Ni has the highest p-value (<0.01).

Table 10. *Result from stepwise MLR for the lake with the Osgood index shallow. Sediment values (mg/kg) are given as dry weight, water concentration in (µg/l), TOC in mg/l and sedimentation rate in cm/y*

Metal	r^2	P	N	Inter-cept	pH	TOC	Sed rate	Fe (wat.)	Al (wat.)	Pb (sed.)	Ni (sed.)
Al	0.71	<0.0001	25	0.85			0.51	0.43			
Co	0.73	<0.001	13	-2.00	-0.21	2.06					
Fe	0.79	<0.0001	27	2.01	-0.33	1.13			0.66		
Mn	0.83	<0.0001	27	1.13	-0.29	2.26					
Ni	0.72	<0.01	11	-2.37		1.93	-0.61				
Ni	0.76	<0.001	13	-0.34	-0.31						1.63
Pb	0.86	<0.0001	13	-11.67		2.77				4.11	
V	0.75	<0.0001	13	1.05	-0.20						

The result differed when analyzing the lakes based on WS: LA resulting in less metals that were possible to model (*Table 11*). The highest r^2 value is in the model for Zn (0.97) and the lowest for Mn (0.61). Common for all three categories of WS:LA models was that a linear relationship was found between Mn and TOC with the highest coefficient in models describing lakes with WS:LA ratio less than 12.5.

Table 11. *Result from multiple stepwise regressions with the data divided depending on WS:LA. Sediment concentrations are given as dry weight, precipitation in mm/y and sediment rate in cm/y and TOC (mg/l)*

Metal	WS:LA	r^2	p	N	Intercept	pH	TOC	Sed rate	Precipitation	Fe (wat.)	Cr (sed.)	Zn (sed.)
Co	<12.5	0.89	<0.001	8	1.41	-0.37						
Cr	<12.5	0.89	<0.002	8	2.42				-0.0010		-1.77	
Mn	<12.5	0.73	<0.01	22	-0.02		1.75					
Al	12.5-25	0.84	<0.0001	16	-0.02		1.00		0.0015			
Co	12.5-25	0.90	<0.001	7	2.86	-0.55						
Mn	12.5-25	0.78	<0.0001	16	-0.66		2.10					
Mn	>25	0.75	<0.001	12	3.93				-0.0038			
Mn	>25	0.65	<0.001	12	-0.92		2.40					
Zn	>25	0.97	<0.02		13.75	-2.18		1.54		-2.69		3.00

4.3 Predictive models

The aim with the predictive models was that they should be based on variables that are easy and simple to measure, such as TOC and pH. Together with the requirement that historical concentrations should be able to be predicted as well.
Of all the general models, Pb was the only one of the studied metals that was possible to predict based only on these two variables. A linear relationship was found between Zn and pH while sedimentation rate and TOC were needed to predict Ni. For predictive models, the reconstructed pH (reference) was used for all years.

4.3.1 Lead

It was possible to predict lead concentration based on pH and TOC only ($r^2 = 0.79$) (*Equation* (1). In the expression, $\log_{10}$ transformed lead concentration an increase of pH has a negative impact on amount of Pb in the water while TOC has positive impact. The model is based on 21 data points.

$$\log(Pb\ \mu g/l) = 0.3875 + (-0.4082) \times pH + 1.57 \times \log(TOC\ mg/l) \qquad (1)$$

The model was applied to 11 of the 17 lakes. In the general models, TOC is based on annual averages, which reduce the variability of multiple measured values during e.g., intense rainfall events. When comparing the measured and the reconstructed TOC it appeared that the measured data was often higher than the predicted data. But to be able to do historical modelling, reconstructed TOC had to be used.

The results are divided into acid and neutral lakes (*Figure 4* and *Figure 5)*). There is a difference in magnitude of Pb in the two types of lakes; the concentration is lower in the neutral lakes compared to the acidic lakes. But it is possible to see the same general trend in both type of lakes, an increase from 1950 with a peak around late 1980's. In Rotehogstjärn, the increase is four times the concentration in 1950.

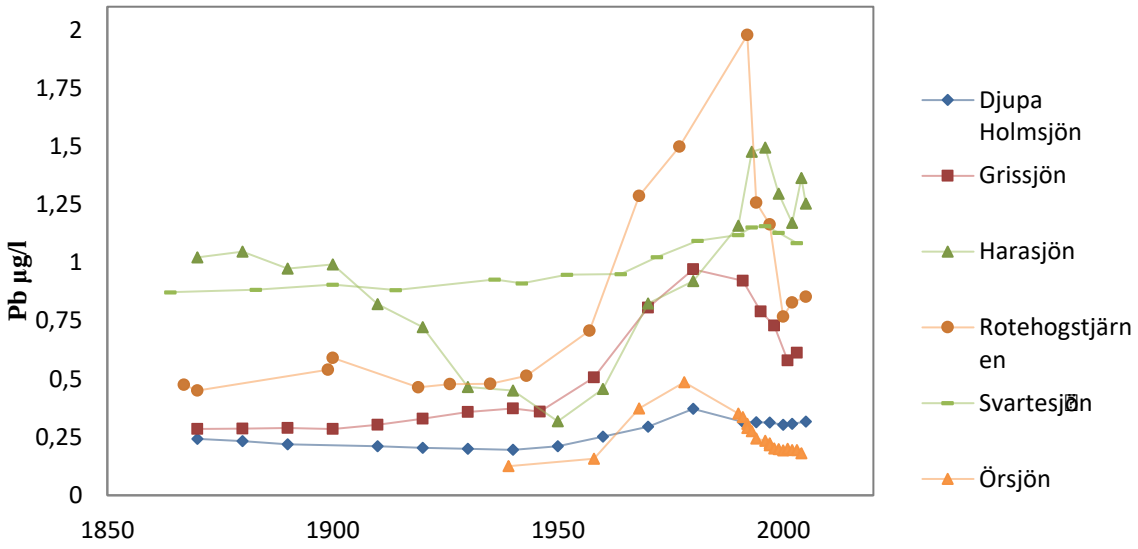


Figure 4. Modeled Pb (ug/L) concentration for acid lakes based on equation 1. In Lake Harasjön there is a decrease in Pb concentration during 1860-1950 and then an increase takes places. The same trend is also shown in Lake Rotehogstjärn and Lake Grissjön during the same time period

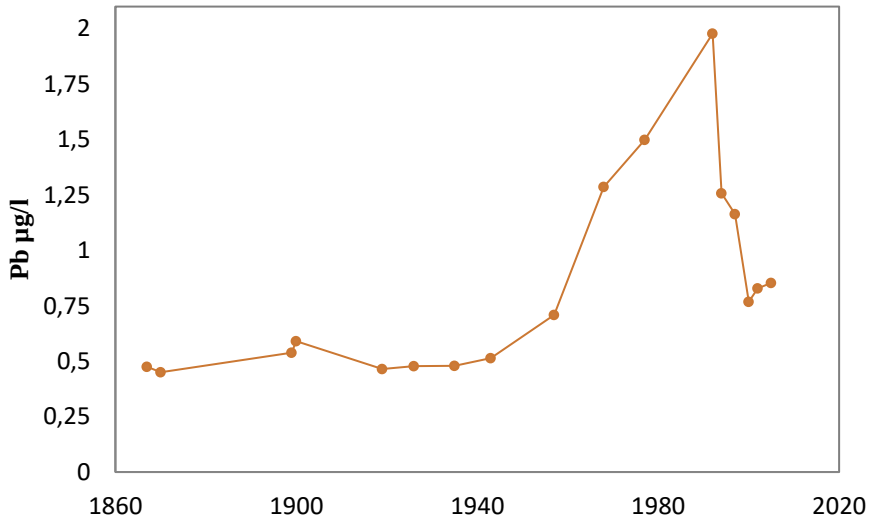


Figure 5. Modelled concentration of Pb (µg/l) in the acid Lake Rotehogstjärn. Between 1935-1992 the concentration of Pb increases four times

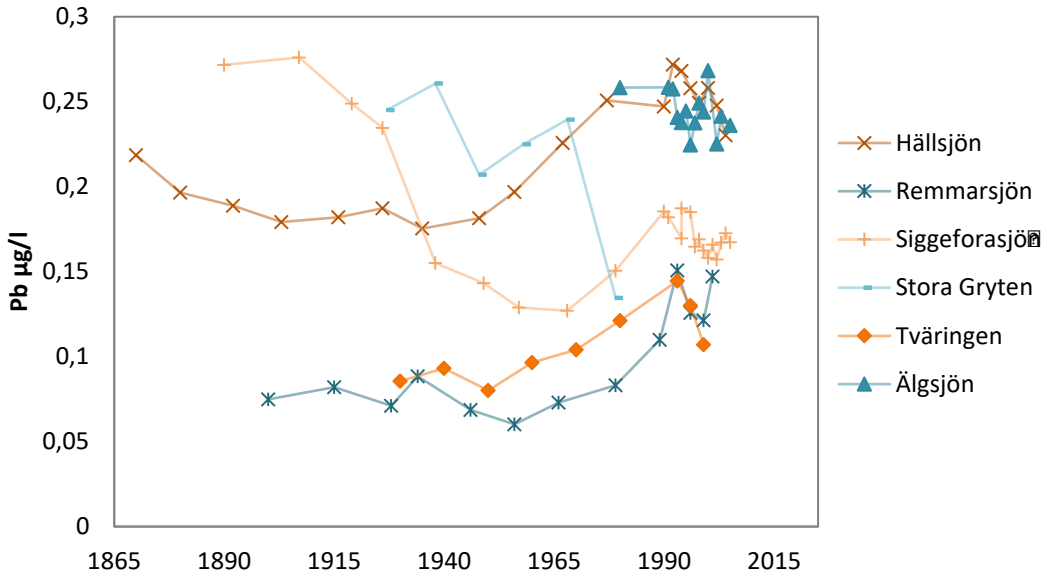


Figure 6. Concentration of Pb (µg/l) model applied to neutral lakes (*Equation 1*).Three of the lakes has increasing concentration during the time period 1940-1990, while Lake Siggeforasjön has a decrease Pb concentration during the same period

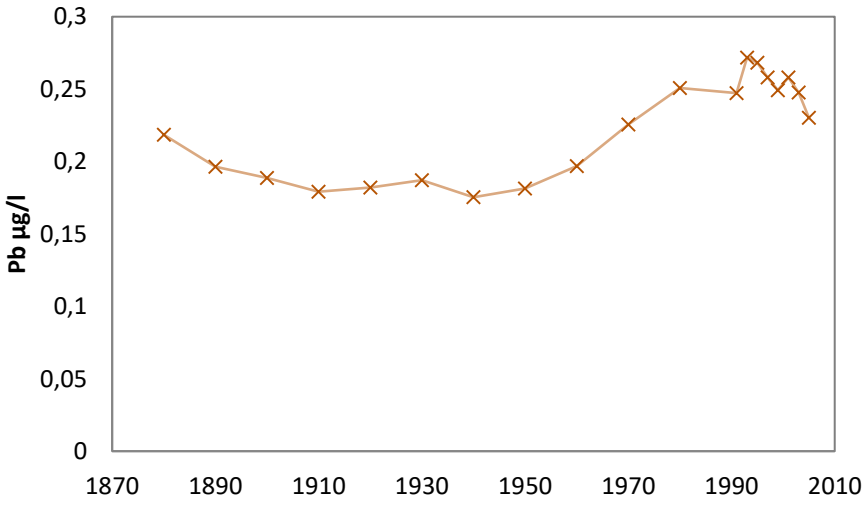


Figure 7. Modelled concentration of Pb (µg/l) in the neutral Lake Hällsjön based on *Equation 1*. There is a slight increase of concentration of Pb in from the 1940 until around 1990, just as in Lake Rotehogstjärn

4.3.2 Zink

The model with highest r^2 value (0.79) had pH, TOC, sedimentation rate, precipitation and Cr concentration in the lake sediment and Al concentration in the lake water as driving variables (*Equation 3*). However, this model can't predict historical concentration because of no available historical records earlier than 1980's of Al concentration in lake water.

$$\log Zn\ (\mu g/l) = 8.84 - 1.30 \times pH + 1.53 \times \log TOC + 0.86 \times sed.rate + 1.53 \times \log Cr(mg/kg\ TS) - 1.94 \times \log Al\ (ug/l) \quad (3)$$

But a linear relationship was also found with pH as the only driving variable (r^2=0.47) (*Equation 4).* Similar to Pb, an increase in pH has negative impact on Zn concentration. The model was built with data points from eight lakes, but has been applied to the eleven lakes with data available for reconstructed pH (*Figure 8* and *Figure 9*).

$$\log\ Zn\ (\mu g/l) = 3.028 + (-0.395) \times pH \quad (4)$$

For Lake Harasjön, Svartesjön, Rotehogstjärnen, Grissjön the concentration of Zn follow a similar trend with a peak in the late 1980's. In the other lakes there was a small peak but not as distinct as in the first mentioned.

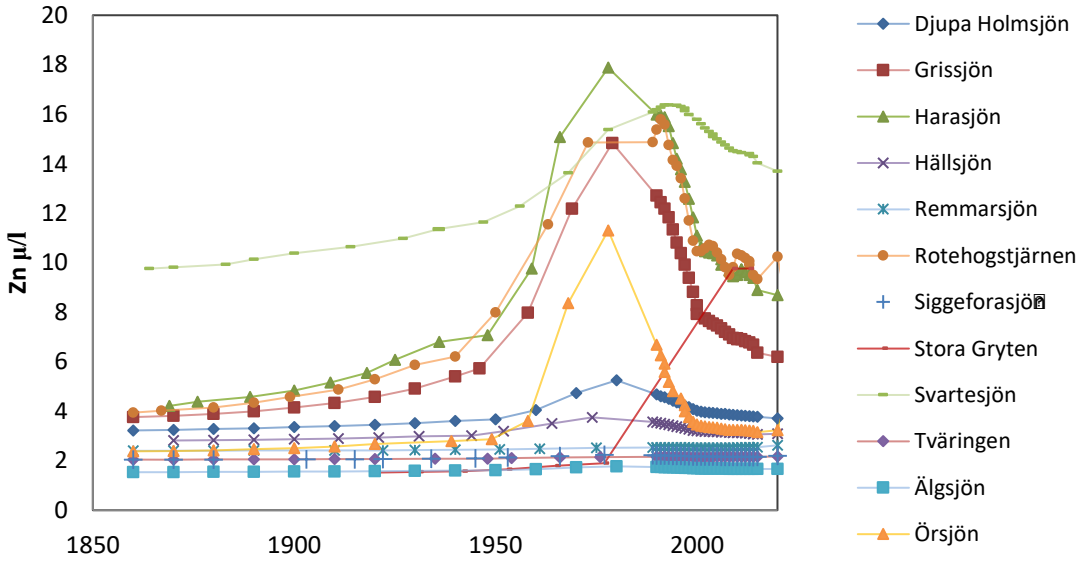


Figure 8. Predicted concentrations of Zn based on *Equation 4.* In most of the lakes an increase, with different magnitude, in Zn concentration takes place with a peak in the late 1980's, following with a decrease right after

Lake Hällsjön and Lake Rotehogstjärn are an example of two lakes where the magnitude of variation in Zn concentration between the lakes was high (*Figure 9*). This is caused by Lake Hällsjön having a higher pH than Lake Rotehogstjärn.

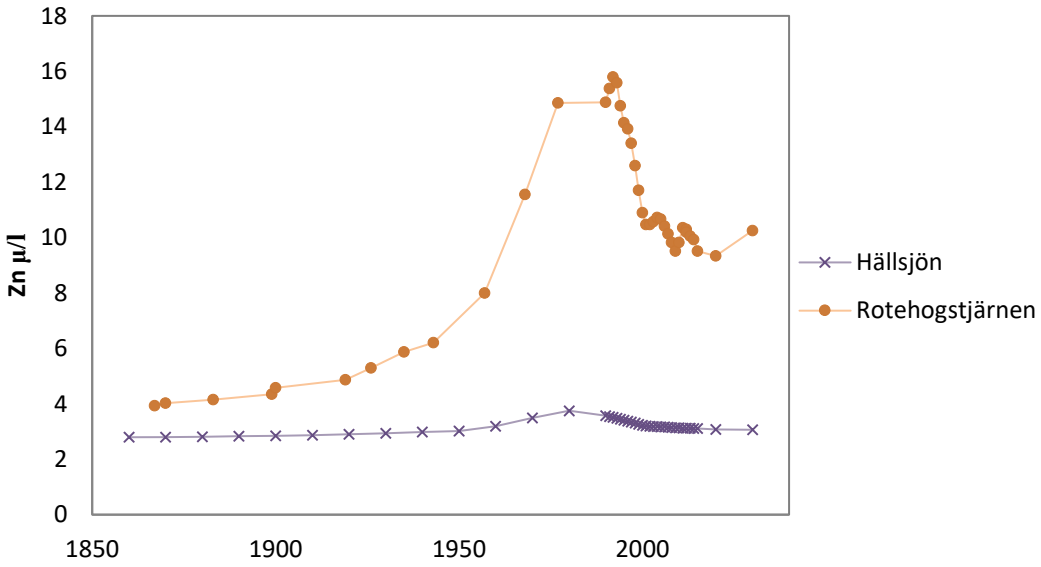


Figure 9. Modelled concentration of Zn (µg/l) in Lake Hällsjön and Lake Rotehogstjärnen. The lakes are an example of the difference in magnitude of Zn concentration in lakes with acid (Rotehogstjärn) and neutral pH (Hällsjön)

4.3.3 Nickel

Ni was possible to predict based on TOC concentration and sedimentation rate (cm/y) (*Equation* (5). The model is based on 15 data points from five lakes and have an r^2 value of 0.73.

$$\log(Ni\ \mu g/l) = (-1.643) + (-0.753) \times Sed\ rate + 1.401 \times \log(TOC\ mg/l) \quad (5)$$

The model was applied to lakes that had yearly matching data with both reconstructed TOC and sediment data. It was possible to see some pattern in the prediction of Ni (*Figure 10*). For Lake Harasjön, Lake Djupa Holmsjön, Lake Tväringen and Lake Remmarsjön it was illustrated as a decrease during the early of 1900's and then shifting to an increase during late 1900's.

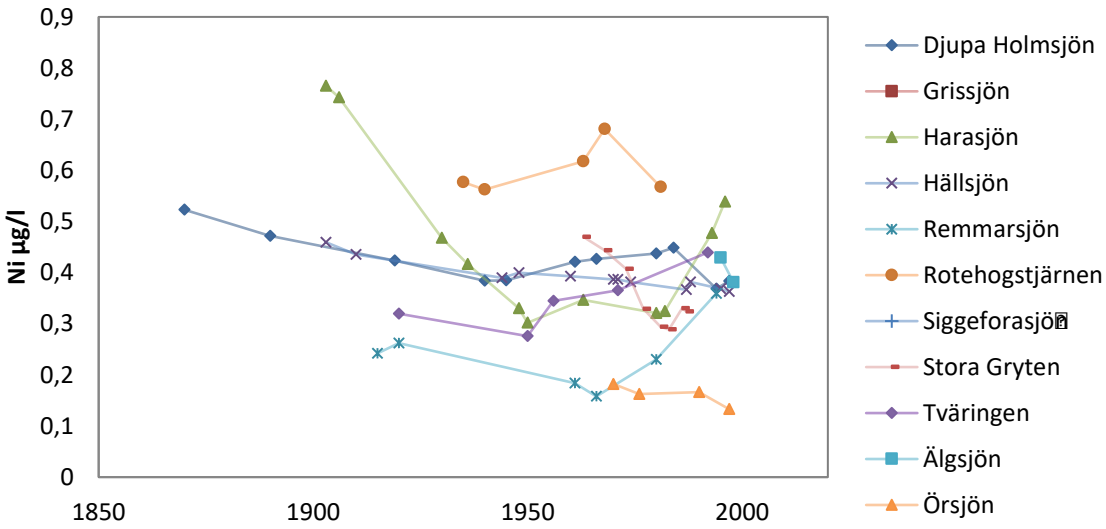


Figure 10. Prediction of Ni concentration in 11 lakes based on *Equation 3*. For Lake Djupa Holmsjön, Lake Harasjön, Lake Tväringen and Lake Remmarsjön there was a pattern with a decrease between early 1900's which shift to an increase after 1950

4.4 Residuals

The residuals from the predictive models were plotted as a method to validate the models (*Figure 11*). If the residuals are randomly distributed through all the x-values, the data are homoscedastic, indicating that a linear regression can be used. In contrast, if the variation is increasing/decreasing with the value of the independent variables, the data is heteroscedastic and linear regression should not be used (Grandin, 2013). For both Pb and Zn the models plotted data seems to be homoscedastic, while for Ni the variation decreases with higher value on the x-axis. However, the amount of data points decreases with higher values, so it was not possible to accurately determine if the data were heteroscedastic or not.

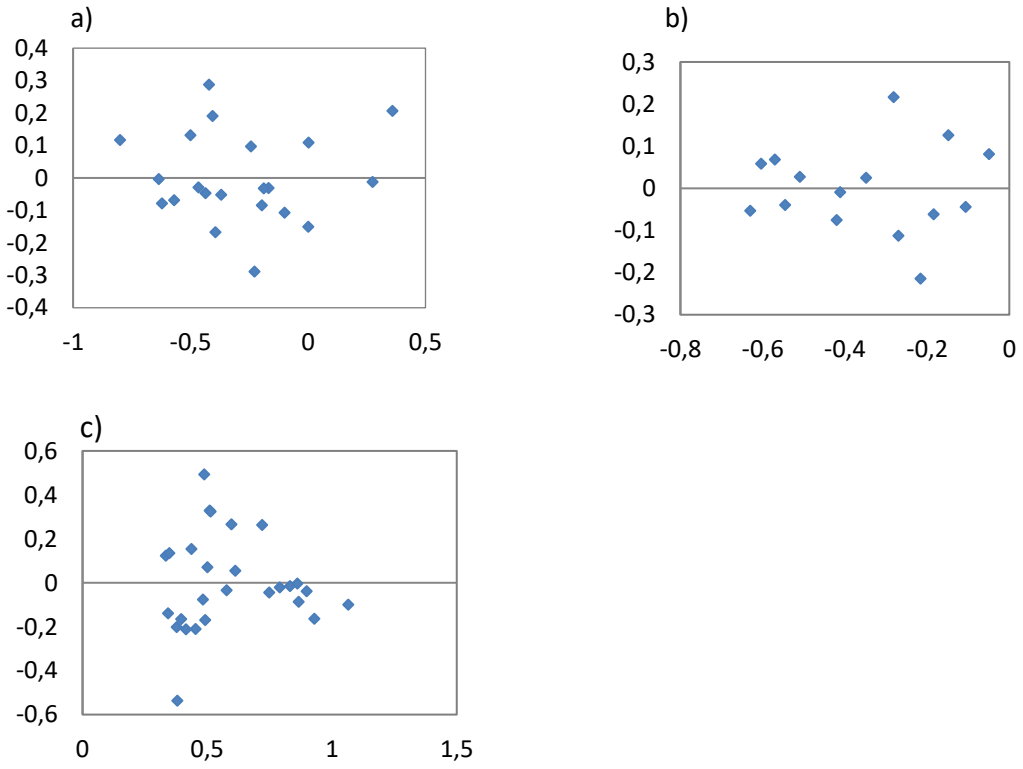


Figure 11. Residuals plotted against predicted values for Pb (a), Ni (b) and Zn (c). The data are log transformed. For both Pb and Zn, the plotted residuals seems to be homoscedastic, while the distribution of Ni residuals decrease with higher value on the x-axes. This could indicate that the data is heteroscedastic- However, the amount of data point decreased so it is not possible to determine

4.5 Comparison of measured and predicted data

The predicted concentrations of the three metals were plotted against the measured to evaluate the models (*Figure 12.* Predicted concentration of $\log_{10}$ Pb (µg/l) plotted against the measured concentration. The line represent if the predicted values would correspond to the measured. In this case the data point are spread on both side of the line which indicate that the models doesn't clearly over- or under estimate the concentration). The straight line in the figure represent if the predicted values would equal the measured values. The distance between the line and the points represent the difference between the models predictions and the measured concentration.

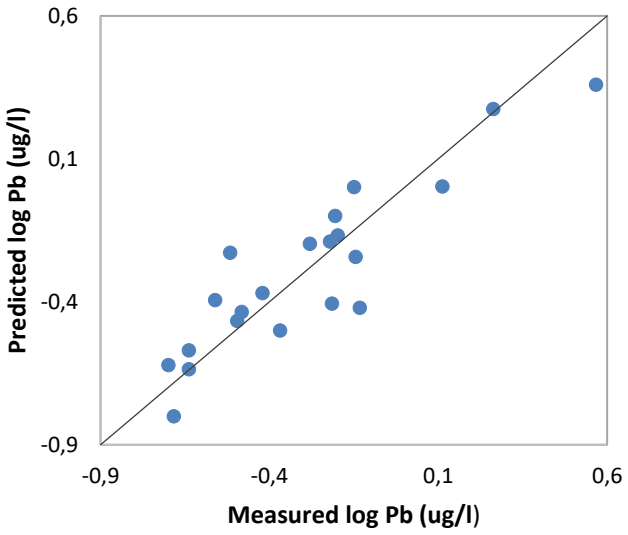
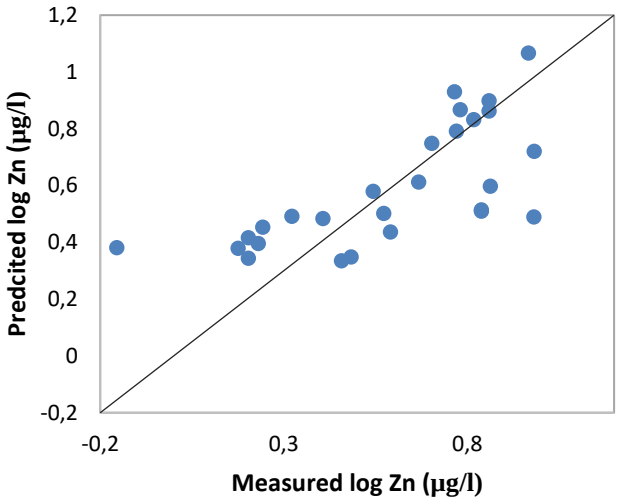


Figure 12. Predicted concentration of $\log_{10}$ Pb (µg/l) plotted against the measured concentration. The line represent if the predicted values would correspond to the measured. In this case the data point are spread on both side of the line which indicate that the models doesn't clearly over- or under estimate the concentration

The Pb model have data points spread on both side of the line (line representing if the predicted values would equal the measure). No clear pattern of over- underestimation is visible. When comparing the predicted concentration of Zn versus the measured concentration the same distribution of plots is visible (*Figure 13).*



Figur 13. Predicted concentration of Zn plotted against the measured concentration. The line represent if the predicted values would correspond to the measured

When the Ni model was plotted against the measured data the distribution looked quite the same as the two other models, with points spread quite close and on both side of the line (*Figur 13*).

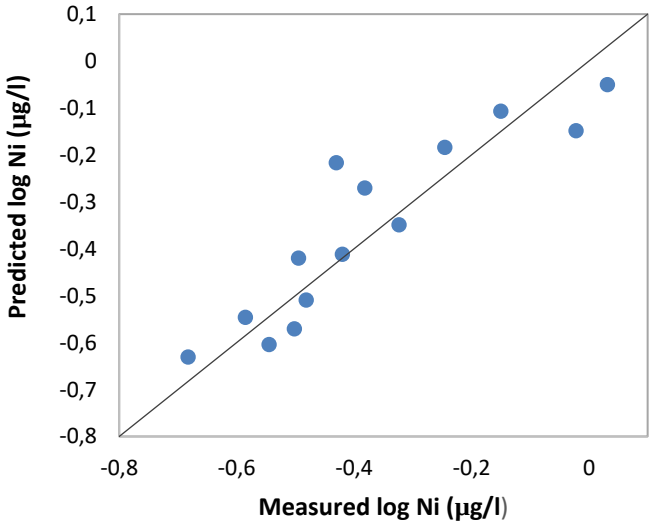


Figure 14 Predicted concentration of Ni (µg/l) plotted against the measured concentration. The straight line represent if the predicted values would correspond exactly to the measured values

4.6 Background concentrations

Both Pb and Zn could be reconstructed back to 1870 and 1860 with exception for some lakes (*Table 12* and *Table 13*). The predicted background concentration of Zn varies in the range of 1.53-9.76 for 11 of the studied lakes.

Table 12. *Predicted background concentration of Zn (µg/l) based on reconstructed pH*

Lake	Year	Zn
Djupa Holmsjön	1860	3.22
Grissjön	1860	3.76
Harasjön	1860	4.12
Hällsjön	1860	2.79
Remmarsjön	1860	2.40
Rotehogstjärnen	1860	3.94
Siggeforasjön	1860	2.04
Svartesjön	1860	9.76
Tväringen	1860	2.04
Älgsjön	1860	1.53
Örsjön	1860	2.38

Regarding Pb concentration the magnitude of variation was lower compared to Zn as the predicted background concentration varied between 0.22-1.02 (magnitude of 0.8).

Table 13. *Predicted background concentration of Pb (µg/l) based on reconstructed TOC and pH*

Lake	Year	Pb
Djupa Holmsjön	1870	0.24
Grissjön	1870	0.28
Harasjön	1870	1.02
Hällsjön	1880	0.22
Remmarsjön	1910	0.07
Rotehogstjärnen	1870	0.47
Siggeforasjön	1900	0.27
Svartesjön	1860	0.87

Ni was only possible to reconstruct in Lake Djupa Holmsjön further back than 1900 and it was 0.52 µg/l. Closest in time then came Lake Harasjön (1903) with an concentration of 0.76 µg/l.

5 Discussion

5.1 General models

The variation in water chemical data between the lakes was high, which is positive when developing a general model. It was possible to construct models for all metals included in the study. The model with highest r^2 value was Zn in lakes with a high WS:LA ratio (small lake area and/or big watershed). Two common parameters for most of the models were pH and TOC. When TOC increases in a lake, it contributes with potential ligands for the metals to create organic complexes with. This can keep the metals dissolved instead of being adsorbed to particles.

When pH is low, the fraction of non-bound metals is high due to competition by protons for surface sites on particles. Cation exchange can also occur and metals bound to colloids can be dissolved due to protons taking their place. This was shown in the results and is also consistent with an earlier study (Köhler, 2010) showing that increasing pH decreases the ratio between filtered metals (the colloidal together with dissolved metal) and total metals (includes dissolved, adsorbed, colloidal) in Swedish lakes (Pb, Fe and Al).

Low pH could be why Lake Harasjön deviated more than the other lakes regarding concentrations of metals (*Table 5*). The lake is acidic which leads to more metals in solution and the internal load/release of metals from sediment can also increase. It also had an Osgood Index classification of "shallow" indicating that it may be polymictic (no or only a weak thermocline). When no thermocline is created there will be more mixing of the water, less oxygen depletion and probably a lower pH at the sediment surface. Lake Harasjön had the second largest cover of wetland area, however, which should instead decrease the metals reaching the lake (especially for organophilic metals) (Lidman et al., 2014). Additional explanation for higher metals concentrations would be that the catchment of Lake Harasjön has an easily weathered soil with high metal content.

According to the models, the amount of Fe in water and sediment influences the concentrations of Al, Zn, Ni, Co and V in the lake water. Colloidal form of iron (<0.45 μm) can act as a surface to bind different metals, especially strong associations have earlier been found between Al and colloidal Fe (Pokrovsky and Schott, 2002).

The multivariate correlation analysis made in this study showed that V, Pb and Al are strongly correlated to Fe concentration in water while for Ni and Zn there was only a very weak correlation. Recent research has also found a similar relationship for Co and Pb (Köhler, 2010). When Fe had negative impact on the metal concentration (decreasing) it may be caused by the metal creating surface complexes with iron hydroxide.

By dividing the lakes based on different chemical and morphological properties, the numbers of possible models increased. These models were not applied to data from other lakes but the results imply that more time should be dedicated to developing models specific to different lake types.

5.2 Predictive models

When applying the constructed models using reconstructed data (pH and TOC), it was possible to predict concentration of Pb and Zn, as well as Ni to a limited extent. During later part of 1900's, most of the lakes had a peak in the predicted concentrations of Pb. The peak is highest for Lake Rotehogstjärn with concentrations reaching 2 µg/l in approximately the late 1980s. This could be caused by either a decrease in pH during this time period or increase of TOC, or in combination with the atmospheric deposition of metals taking place at this time (Rühling and Tyler, 2001).

When applying the Zn model to reconstructed data, the results for almost all lakes followed the same pattern, due to pH being the only parameter in the expression (decreasing pH increases the metal concentration). The peak takes place around late 1980´s, which corresponds to acidification effects caused by industrial activity.

The prediction of Ni concentrations on the other hand didn't have the same distinct pattern over time compared to Pb and Zn. Four lakes (Harasjön, Djupa Holmsjön, Tväringen and Remmarsjön) had a decrease in Ni following by an increase after 1950's but when looking at their chemical and morphological parameters no common denominator was found except for both acid lakes (Harasjön and Djupa Holmsjön) have a greater magnitude of their decrease than the two neutral lakes. Lake Djupa Holmsjön is the only one of the four mention lakes that also has a decrease during the 1990's.

Stratification can lead to oxygen depletion in the deeper layer of the lakes, which cause reducing conditions. Both Pb and Zn are classified as B-type of metal cations, indicating that they prefer soft ligands (S for example), which is favoured by reducing conditions (stratified lakes). To the contrary, if the metals are bound to organic material forming an organometallic compound, they are more strongly bound compared to complexation. The later of these phenomena could appear more often in polymictic lakes.

5.3 Background concentrations

Comparison between measured and predicted values showed that they all had data points spread quite even on both side of the line. Which indicated that none of the models constantly over- or underestimate the metals concentration. But for Zn tho a small majority was found on the left side of the line which could indicate a small overestimation of Zn in the lake water. One reason for this could be that a change in pH has a greater effect on Zn than on Pb and Ni, due to pH being the only parameter in the Zn model. This could be explained through Zn being more common as free ion form than Ni and Pb, which could make Zn simpler to model. Pb on the other hand form strong complexes together with humic substances and oxides (Gustafsson et al., 2007), which explains the addition of TOC as model parameter. Ni has common properties to Zn, but at higher pH and if Al is present it can more easily precipitate compared to Zn (Gustafsson et al., 2007). In the predictive models produced in this study, Al is not present as a parameter. The reason for this could be that the lake used in the modelling was even spread between acidic and neutral lakes which reduced the impact of Al.

The residuals were also analyzed for Pb, Zn and Ni models. The distribution was random for both Pb and Ni while the Zn residuals were more tightly clustered at higher concentrations. This could have been explained by fewer data points, but the low amount of data makes it difficult to evaluate the result.

Two predictive models were constructed for Zn (*Equation 3 and 4*). The first one (*Equation 3)* consists of more parameters and had higher r^2 value compared to *Equation 4*. The second model (*Equation 4)* had lower r^2, and describes a linear relationship between Zn and pH and can be used to describe historical concentration in contrast to *Equation 3* due to the fact that there are already established models able to predict the historical concentration of pH.

The result from the predicted background concentrations for all three metals was higher than the estimated values from SEPA for non-acid lakes (*Table 2*). It was not possible to go as far back as 1860 for all lakes using the Pb model due to lack of reconstructed TOC and/or pH so far back time. The predicted background concentration of Zn however was higher for all lakes except Lake Älgsjön, than SEPA's comparison values. One of the lakes (Svartesjön) was almost 5 times higher than the regional background concentration for South of Sweden. Lake Svartesjön is one of the lakes with the highest percentage of wetlands covering the watershed which corresponds to earlier research (Lidman et al., 2014) that has shown a negative correlation between wetland coverage and stream water concentration of trace element.

For Ni it was only possible to go as far back as 1870 for one lake (Djupa Holmsjön), Lake Djupa Holmsjön had, just as with Pb and Zn, more than twice as high concentration as the SEPA comparison values for non-acid lakes .

The overall high modelled background concentration raises the question to divide the lakes based on pH before constructing the models (Table *8*) to see how this would impact the parameters in the model.

By underestimating the concentrations of metals in a lake when performing environmental assessment there is a risk to classify a lake as more affected by anthropogenic emission than it actually is. Which in itself leads to no harm, but it may result in environmental monitoring goals are set to high and not possible to reach.

5.4 Model limitations

The distributions of data was uneven between the lakes (*Table* 5 and Appendices - Table *16*), which could cause some lakes to have higher influence on the models than others. The solution to minimize the impact of certain lakes could be to only use lakes with the same amount of monitored data. Still, in this case, the amount of data was low from the beginning so all available data was used to be able to see if it was possible create any model.

As always when working with modelled data as input variables, the potential errors made in the first model are included in the next model. This increases the uncertainty

of the results. Research also shows that metals in surface water has a high temporally variance which makes it different to model in high
However, this project was a good first step for predicting metal concentrations based on easily measured parameters such as pH and TOC, which have a long history of monitoring and are parameters that are possible to reconstruct historically.

5.5 Further work

Research predicts that TOC concentration will increase in the future (Cunningham et al., 2011; Rosén, 2005). Confirming this, Huser et al. (2011 and 2012) showed that TOC has increased in Swedish running waters over the last few decades, and is expected to continue increasing in the future. Combined with the results from this study, this would suggest that concentration of metals in lake water will increase in the future. For metals that bind strongly with TOC (Pb, Zn, Cr), this means that concentrations in lakes may increase without any impact from anthropogenic sources. But at the same time many lakes are recovering from the acidification during the 1980's which could decrease the effect of pH.

The models constructed in this study should not yet be applied for evaluating water quality criteria. However, the area of topic should be further investigated and seen as an indicative of the direction of the monitoring of Swedish lakes. As further work, the data set should be increased to include more lakes and the same procedure could be done, for metal concentrations in the sediment. Through this approach it would be possible to compare the result against sediment samples as a way to evaluate the models.

6 Conclusions

This study showed that it is possible to estimate historical concentrations of some metals using a few, easy to measure, model parameters in the water and sediment of lakes. This could provide a better method for estimated background concentrations compared using current concentrations from minimally impacted lakes, because all lakes are affected to some extent by anthropogenic emissions of metals (through deposition). To improve the models in this study, more lake sediment cores could be analysed and used. In addition, more attention is needed to this subject to improve the predictive modelling approach of metals in lakes, which in turn would improve the decision making and sampling design for environmental monitoring.

The conclusions from this study are:

- It was possible to create models describing metal concentrations in a lake based only on available data for Al, Cu, Cr, Co, Fe, Mn, Pb, Ni, Zn and V.

- It was also possible to model background concentration for Pb, Zn and Ni but the results should be evaluated further and the models tested by applying them to a larger number of lakes.

7 References

Appleby, P.., Oldfield, F., 1978. The calculation of 210Pb dates assuming a constant rate of supply of unsupported 210Pb to the sediment. Catena 1978, 1–5.

Berggren Kleja, D., Elert, M., Gustafsson, J.P., Jarvis, N., Norrström, A.-C., 2006. Metallers mobilitet i mark (No. 5536). Stockholm : Naturvårdsverket, Stockholm.

Boyle, J., 2001. Redox remobilization and the heavy metal record in lake sediments: a modelling approach 2001, 423–431.

Cooke, G.D., Welch, E.B., Peterson, S., Newroth, P., 1993. Restoration and Management of Lakes and Reservoirs, Second Edition. CRC Press.

Cosby, B.., Hornberger, G.., Galloway, J.., Wright, R.., 1985a. Modelling the effects of acid deposition: assessment of a lumped-parameter model of soil water and streamwater chemistry. Water Res. 1985, 51–63.

Cosby, B.., Hornberger, G.., Galloway, J.., Wright, R.., 1985b. Modelling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. Water Res. 1985, 1591–1601.

Cosby, B.., Hornberger, G.., Galloway, J.., Wright, R.., 1985c. Time scales of catchment acidification: a quantitative model for estimating freshwater acidification. Environ. Sci. Technol. 1985, 1144–1149.

CRU [WWW Document], 2008. . CEDA Catalouge Site. URL http://catalogue.ceda.ac.uk/uuid/3f8944800cc48e1cbc29a5ee12d8542d

Cunningham, L., Bishop, K., Mettävainio, E., Rosén, P., 2011. Paleoecological evidence of major declines in total organic carbon concentrations since the nineteenth century in four nemoboreal lakes. J. Paleolimnol. 45, 507–518. doi:10.1007/s10933-010-9420-x

EUR-Lex - 32000L0060 - SV [WWW Document], 2000. . Eur. Gemenskapernas Off. Tidn. Nr 327 22122000 0001 - 0073. URL http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32000L0060:SV:HTML (accessed 5.26.15).

Fölster, J., Hallstan, S., Johnson, R.K., 2014. Utvärdering av de nationella miljöövervakningsprogrammen av sjöar - Trendsjöar och Sjöomdrev (No. 2014:3). Institutionen för vatten och miljö, Uppsala.

Futter, M.N., Valinia, S., Löfgren, S., Köhler, S.J., Fölster, J., 2014. Long-term trends in water chemistry of acid-sensitive Swedish lakes show slow recovery from historic acidification. AMBIO 43, 77–90. doi:10.1007/s13280-014-0563-2

Grandin, U., 2013. Dataanalys och hypotesprövnng för statistikanvändare. Naturvårdsverket, Uppsala.

Gustafsson, J.-P., Jacks, G., Simonsson, M., Nilsson, I., 2007. Soil and water chemistry. KTH, Stockholm.

Håkanson, L., 1995. Optimal size of predictive models. Ecol. Model. 78, 195 – 204. doi:http://dx.doi.org/10.1016/0304-3800(93)E0103-A
Håkanson, L., 1983. Principles of lake sedimentology. Springer-Verlag, Berlin ; New York.
Hart, B.T., 1982. Uptake of trace metals by sediments and suspended particulates: a review, in: Sly, P.G. (Ed.), Sediment/Freshwater Interaction. Springer Netherlands, Dordrecht, pp. 299–313.
Huser, B.J., Fölster, J., Köhler, S.J., 2012. Lead, zinc, and chromium concentrations in acidic headwater streams in Sweden explained by chemical, climatic, and land-use variations. Biogeosciences 9, 4323–4335. doi:10.5194/bg-9-4323-2012
Johansson, K., Björkvald, L., Herbert, R., Wällstedt, T., 2009. Bakgrundshalter av metaller i Svenska inlands- och kustvatten. SLU, Uppsala.
Köhler, S.J., 2010. Comparing filtered and unfiltered metal concentrations in some Swedish surface waters (No. 2010:04). Department of Aquatic Sciences and Assessment, Uppsala.
Kretzschmar, R., Schafer, T., 2005. Metal Retention and Transport on Colloidal Particles in the Environment. Elements 1, 205–210. doi:10.2113/gselements.1.4.205
Lidman, F., Köhler, S.J., Mörth, C.-M., Laudon, H., 2014. Metal Transport in the Boreal Landscape—The Role of Wetlands and the Affinity for Organic Matter. Environ. Sci. Technol. 48, 3783–3790. doi:10.1021/es4045506
Lindström, M., 2000. Predictive Modelling of Heavy Metals in Urban Lakes.
Mason, R.P., 2013. Trace Metals in Aquatic Systems. Wiley-Blackwell, Chichester, West Sussex.
McBride, M.B., 1994. Environmental Chemistry of Soils. Oxford University Press, Oxford.
Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333, 134–139. doi:10.1038/333134a0
Olid, C., Nilsson, M.B., Eriksson, T., Klaminder, J., 2014. The effects of temperature and nitrogen and sulfur additions on carbon accumulation in a nutrient-poor boreal mire: Decadal effects assessed using ^{210}Pb peat chronologies. J. Geophys. Res. Biogeosciences 119, 392–403. doi:10.1002/2013JG002365
Övervakning enl. vattendirektivet [WWW Document], n.d. URL http://projektwebbar.lansstyrelsen.se/viss/Sv/detta-beskrivs-i-viss/miljoovervakning/Pages/overvakning-enl-vattendirektivet.aspx (accessed 5.26.15).
Pérez-Fuentetaja, A., McQueen, D.J., Dillon, P.J., Yan, N.D., 1999. Significance of dissolved organic carbon in the prediction of thermocline depth in small Canadian shield lakes 33, 127–133. doi:10.1023/A:1009998118504
Pokrovsky, O.S., Schott, J., 2002. Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). Chem. Geol. 190, 141–179. doi:10.1016/S0009-2541(02)00115-8

Rosén, P., 2005. Total Organic Carbon (TOC) of Lake Water During the Holocene Inferred from Lake Sediments and Near-infrared Spectroscopy (NIRS) in Eight Lakes from Northern Sweden. Biogeochemistry 76, 503–516. doi:10.1007/s10533-005-8829-1

Rühling, Å., Tyler, G., 2001. Changes in Atmospheric Deposition Rates of Heavy Metals in Sweden A Summary of Nationwide Swedish Surveys in 1968/70 – 1995. Water Air Soil Pollut. Focus 1, 311–323. doi:10.1023/A:1017584928458

Rühling, Å., Tyler, G., 1971. Regional differences in the deposition of heavy metals over Scandinavia. Reg. Differ. Depos. Heavy Met. Scand. Aug, 497–507.

SEPA, 2010. Status, potential and quality requirements for lakes, watercourses, coastal and transitional waters, 1st ed. Swedish Environmental Protection Agency, Stockholm.

Sparks, D.L., 2005. Toxic Metals in the Environment: The Role of Surfaces. Elements 1, 193–197. doi:10.2113/gselements.1.4.193

Stoddard, J.L., Larsen, D.P., Hawkins, C.P., Johnson, R.K., Norris, R.H., 2006. Setting expectations for the ecological condition of streams: The concept of reference condition. Ecol. Appl. 16, 1267–1276. doi:10.1890/1051-0761(2006)016[1267:SEFTEC]2.0.CO;2

Stumm, W., 1996. Aquatic chemistry: chemical equilibria and rates in natural waters, 3rd ed. ed, Environmental science and technology. Wiley, New York.

Swedish Environmental Protection Agency, n.d. Beskrivning av delprogrammet Trendsjöar.

Wiederholm, T., 2000. Sjöar och vattendrag: Bedömningsgrunder för miljökvalitet : Bakgrundsrapport 1 : kemiska och fysikaliska parametrar. Naturvårdsverket Förlag.

Appendix 1

Table 14. *Comparison between replicates of ICP-MS measurement and ICP_AES. Unit mg/kg TS*

Method	Lake	Sed. sec-tion	Al	Fe	Mn	Cu	Zn	Pb	Cd	Cr	Ni	Co	As	V
ICP-MS	Brunnsjön	0-2	16450	27960	141	27,3	83,5	106	1,79	16	12.1	10.1	6.62	68.6
ICP-AES	Brunnsjön	0-2	17783	24873	166	27.6	99.8	107.4	3	14.7	10.85	10.3	11.6	64.5
ICP-MS	Brunnsjön	30-32	10230	12750	253	20.5	51.3	33.1	0.58	10.1	6.66	3.47	3.7	30.9
ICP-AES	Brunnsjön	30-32	10524	12371	255	19.5	77.5	33.5	1.1	9.25	5.72	3.92	7.2	25.9
ICP-MS	Bysjön	2-4	27620	45880	1231	26.5	244	74.1	1.2	30.8	23.7	17.9	5.8	67
ICP-AES	Bysjön	2-4	31242	43527	1161	23.1	231.4	70.7	3.2	25.99	19.41	18.77	7.39	54.5
ICP-MS	Pahajärvi	0-2	14730	116300	1491	29.8	143	64.4	1.2	40	16.3	14.5	8.05	63.8
ICP-AES	Pahajärvi	0-2	11930	96720	1215	23.1	138.6	52.1	5.6	28.867	11.4	10.9	8.5	43.4

Table 15. *Result from multivariate correlation analysis. Concentrations are log transformed. Metals without units are in mg/kg*

	Sed rate	Precipitation	pH	Al	Fe	Mn	Cu	Zn	Pb	Cr	Ni	Co	As	V
Sed Rate	1	-0.45	0.40	0.41	0.28	0.31	-0.12	0.37	-0.25	0.07	-0.14	0.15	-0.03	0.23
Precipitation	-0.45	1.00	-0.69	-0.51	-0.44	-0.55	-0.06	-0.27	-0.05	-0.54	-0.22	-0.38	-0.20	-0.40
pH	0.40	-0.69	1	0.74	0.47	0.72	-0.21	0.36	-0.27	0.69	0.38	0.54	0.08	0.48
Al	0.41	-0.51	0.74	1	0.39	0.59	-0.25	0.47	-0.37	0.78	0.47	0.69	-0.07	0.72
Fe	0.28	-0.44	0.47	0.39	1	0.80	0.25	-0.07	-0.16	0.39	-0.10	0.65	0.59	0.70
Mn	0.31	-0.55	0.72	0.59	0.80	1	0.01	0.16	-0.33	0.64	0.20	0.70	0.31	0.73
Cu	-0.12	-0.06	-0.21	-0.25	0.25	0.01	1	-0.14	0.41	0.02	0.04	0.13	0.20	-0.02
Zn	0.37	-0.27	0.36	0.47	-0.07	0.16	-0.14	1	-0.18	0.36	0.51	0.28	-0.09	0.06
Pb	-0.25	-0.05	-0.27	-0.37	-0.16	-0.33	0.41	-0.18	1	-0.18	-0.14	-0.18	-0.09	-0.11
Cr	0.07	-0.54	0.69	0.78	0.39	0.64	0.02	0.36	-0.18	1	0.69	0.70	-0.09	0.67
Ni	-0.14	-0.22	0.38	0.47	-0.10	0.20	0.04	0.51	-0.14	0.69	1	0.52	-0.22	0.14
Co	0.15	-0.38	0.54	0.69	0.65	0.70	0.13	0.28	-0.18	0.70	0.52	1	0.27	0.73
As	-0.03	-0.20	0.08	-0.07	0.59	0.31	0.20	-0.09	-0.09	-0.09	-0.22	0.27	1	0.13
V	0.23	-0.40	0.48	0.72	0.70	0.73	-0.02	0.06	-0.11	0.67	0.14	0.73	0.13	1
TOC mg/l	0.29	0.07	0.11	0.30	-0.06	0.28	-0.42	0.50	-0.58	0.17	0.22	0.21	-0.22	0.15
Fe µg/l	0.12	0.47	-0.45	-0.20	-0.01	-0.06	-0.23	0.12	-0.38	-0.36	-0.23	-0.09	0.02	-0.03
Mn µg/l	0.32	0.16	-0.15	0.08	0.14	0.19	-0.26	0.25	-0.32	-0.21	-0.11	0.09	-0.03	0.14
Cu µg/l	-0.16	-0.20	0.26	0.24	0.34	0.47	-0.15	0.15	-0.07	0.41	0.24	0.23	0.14	0.39
Zn µg/l	-0.47	0.45	-0.70	-0.62	-0.45	-0.57	0.46	-0.37	0.50	-0.37	-0.11	-0.34	-0.17	-0.24
Al_s µg/l	0.19	0.44	-0.46	0.00	-0.19	-0.22	-0.14	0.17	-0.32	-0.29	-0.10	-0.02	0.02	-0.04

Pb µg/l	-0.09	0.59	-0.71	-0.78	-0.57	-0.36	0.10	-0.13	-0.08	-0.78	-0.27	-0.72	-0.28	-0.59
Cr µg/l	0.13	-0.11	0.06	0.16	-0.06	0.22	-0.44	0.29	-0.63	0.15	0.34	0.10	0.09	0.03
Ni µg/l	-0.45	0.40	-0.17	0.00	-0.47	-0.11	0.06	0.25	-0.48	0.08	0.65	0.05	-0.46	-0.41
Co µg/l	-0.39	0.73	-0.78	-0.48	-0.70	-0.65	0.12	-0.25	-0.10	-0.50	0.05	-0.41	-0.69	-0.48
V µg/l	0.35	0.28	-0.31	-0.25	-0.22	0.05	-0.53	0.03	-0.64	-0.34	-0.11	-0.37	-0.11	-0.14

Appendix 2

Table 16. *Different groups and lakes affiliation, N represent amount of data rows for each lake. The limits for acid lake are pH< 6. As seen in the table some lakes contribute with one data point while other with 11 at most. This is caused by the shortage of overlapping time series of sediment cores and water chemical data*

Lake	Osgood Index	Acidic-Neutral	WS: LA	N
Allgjuttern	Deep	neutral	7.0	3
Djupa Holmsjön	Deep	acidic	11.6	2
Grissjön	Deep	acidic	6.7	3
Harasjön	shallow	acidic	9.8	4
Hällsjön	Deep	neutral	7.1	5
Remmarsjön	shallow	neutral	91.5	1
Rotehogstjärnen	Deep	acidic	21.7	5
Siggeforasjön	shallow	neutral	30.6	11
Stora Envättern	shallow	neutral	3.8	1
Stora Gryten	shallow	neutral	18.1	6
Svartesjön	Deep	acidic	13.9	1
Svinarydsjön	Deep	acidic	9.9	1
Tväringen	shallow	neutral	22.5	1
Tärnan	shallow	neutral	12.7	1
Älgsjön	Deep	neutral	14.0	2
Örsjön	Deep	acidic	4.5	2
Övre Skärsjön	shallow	acidic	5.2	2